REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT DATE	3. DATES COVERED *(From - To)*
2/19/03	Final Project Report	2/1/1991 - 9/30/2002

4. TITLE AND SUBTITLE
Mechanisms of Metal Contact Formation on Molecular Films

5a. CONTRACT NUMBER

5b. GRANT NUMBER
N00014-91-J-1410

5c. PROGRAM ELEMENT NUMBER

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release

20030303 140

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The central aim of our work was to gain a fundamental understanding of the interaction of metal atoms with organic monolayers. This information is crucial to theburgeoning fields of molecular and organic electronics so that low power electronic devices can easily be designed. These systems are relevant not only for molecular/organic electronics but also in organometallic and polymer chemistry.

15. SUBJECT TERMS
SIMS, XPS, IRS

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
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					19b. TELEPONE NUMBER *(Include area code)* 814-863-0001

Molecular Fabrication of Nanoscale Composites

FINAL REPORT

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February 2003

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Contract No: N00014-91-J-1410

Progress

The central aim of our work is to gain a fundamental understanding of the interaction of metal atoms with organic monolayers. This information is crucial to the burgeoning fields of molecular and organic electronics so that low power electronic devices can easily be designed. These systems are relevant not only for molecular/organic electronics but also in organometallic and polymer chemistry.

The most recent work has concentrated on two areas. In the first we have employed a model monolayer, a methoxy terminated alkanethiol, to investigate how the reactivity of different metals affects the formation of contacts. The metals chosen are titanium, calcium, magnesium, aluminum, copper, silver and gold, and are all commonly used contacts in either microelectronics or polymer light emitting diodes. Several papers are in preparation:

1) A. V. Walker, T. B. Tighe, M. D. Reinard, B. C. Haynie, D. L. Allara, N. Winograd, "Solvation of Zero-Valent Metals in Organic Thin Films", *Chem. Phys. Lett.*, submitted.

Abstract: Aluminum, copper and silver atoms are found to form a weakly solvated quasi-isotropic layer when vapor-deposited onto methoxy groups exposed at the surface of a hexadecanethiolate self-assembled monolayer on Au {111}. The nature of the interactions was revealed using SIMS, XPS and IRS, and supported by DFT calculations. This method complements 3-dimensional gas phase cluster experiments by providing an approach for controlling solvation geometry and bonding via the molecular parameters of the monolayer. The results are discussed in terms of their applicability to the design of controlled interfaces, particularly metal contacts in molecular electronic devices.

2) A. V. Walker, T. B. Tighe, O. Cabarcos, M. D. Reinard, B. C. Haynie, D. L. Allara and N. Winograd, "The Dynamics of Metal Penetration Through Methoxy-Terminated Organic Monolayers", *J. Am. Chem. Soc.*, in preparation.

Abstract: We have studied the interaction of Al, Cu, Ag and Au with a methoxy-terminated SAM, $HS(CH_2)_{16}OCH_3$, chemisorbed on a polycrystalline Au{111} surface using time-of-flight secondary ion mass spectrometry, infrared reflection spectroscopy and x-ray photoelectron spectroscopy. For Cu and Ag deposition the metal atoms partition into competitive paths: penetration to the S/substrate interface, and solvation-like interaction with the terminal group. Deposited Au atoms penetrate to the Au/S interface and do not interact with the terminal group. The penetration of the metal atoms to the S/substrate interface causes configurational disorder in the SAM layer and continues even at high metal deposition coverages. In contrast, previous results show that Al atom penetration to the Au/S interface ceases after ~1:1 Al:Au layer has been attained. Using supporting calculations, we demonstrate that these results can be explained in terms of dynamic hopping of metal-thiolate moieties across the surface, which open diffusion channels to the S/substrate interface. Al-thiolate moieties have a higher barrier to lateral diffusion than Au-thiolate, greatly reducing/ stopping the formation of transient defects which leads to the closing of the penetration channel. In contrast, Ag-thiolate and Cu-thiolate groups do not have higher activation energies for lateral diffusion than Au-thiolate moieties and hence the penetration channels remain open.

3) A.V. Walker, T. B. Tighe, L. Dake, B.C. Haynie, D. L. Allara, N. Winograd, "The Interaction of Vapor-Deposited Ca and Ti with Methoxy-Terminated Alkanethiols", *J. Phys. Chem. B*, in preparation.

Abstract: To fully characterize the interaction of vapor-deposited Ti and Ca with a $-OCH_3$ terminated alkanethiol monolayer on Au {111}, we have employed a multi-technique approach using time-of-flight secondary ion mass spectrometry (ToF SIMS) and infrared spectroscopy (IRS). We observe that the metal atoms simultaneously penetrate to the Au/S interface, react with the methoxy terminal group and react with the methylene backbone. This leads to the formation of M-O and M-C bonds, where M = Ti, Ca. The reaction proceeds via attack of the $-OCH_3$ group followed by reaction with the methylene backbone to form calcium and titanium carbide. Titanium is more reactive than Ca. In contrast to Ti, Ca initially reacts with two $-OCH_3$ groups to form an organometallic structure.

4) A. V. Walker, T. B. Tighe, O. Cabarcos, B. C. Haynie, D. L. Allara, N. Winograd, "The Dynamics of Interaction of Magnesium Atoms on Methoxy-Terminated Self-Assembled Monolayers: An Example of a Reactive Metal with a Low Sticking Probability", *J. Phys. Chem. B*, in preparation.

Abstract: We have studied the interaction of magnesium with a methoxy terminated self-assembled monolayer (SAM), $HS(CH_2)_{16}OCH_3$, chemisorbed on a polycrystalline Au {111} surface using time-of-flight secondary ion mass spectrometry and infrared reflection spectroscopy. Magnesium has a very low sticking probability, $\sim 2 \times 10^{-4}$, at room temperature. Upon adsorption on the SAM, Mg inserts into the $-OCH_3$ group to form an Mg-O-R complex. We estimate the activation energy for the complexation is ~ 43 kJ mol^{-1}. As the Mg reaction with the $-OCH_3$ group proceeds, the methylene chains re-orient on the surface to become

more upright. Between θ_{Mg} ~ 250 and 375, magnesium forms a metallic overlayer. We also compare these results with interaction of aluminum with a methoxy-terminated SAM.

In the second area of research, we have performed the first studies of metal contact formation on a molecular wire monolayer. In our first experiments, we studied the interaction of a molecular wire, 4-[4'-(phenylethynyl)-phenylethynyl]-benzenethiol, which consists of three phenyl rings separated by C≡C bonds, with two common electronic contacts, Ti and Au. Again we observed that Ti destroys the monolayer and Au penetrates through the monolayer causing shorts. In a second series of experiments we examined the interaction of Al, Cu and Ag with the wire molecules. Upon deposition of Ag and, we observed that M-phenyl moieties formed, where M = Cu and Ag. Concomitant with this, the metal atoms also penetrate through the monolayer to the Au/S interface. The penetration of metal atoms continued at all deposited metal coverages studied. In contrast, deposited Al penetrates through the monolayer without interacting with the phenyl groups. At higher Al coverages, a metallic Al overlayer forms. Both iron and chromium atoms form ferrocene-type organometallic structures. To test whether we could form such structures using wire monolayers, preventing diffusion of metal atoms to the Au/S interface, we deposited Fe and Cr on the wire monolayers. Upon deposition of iron, we observe the formation of Fe-phenyl moieties indicating that Fe has interacted with the phenyl rings of the molecular wire to form structures that are similar to ferrocene. For Cr deposition, we observe that the monolayer structure is destroyed.

In summary, the formation of metallic contacts with organic molecules is very complex. However, our work provides a framework for controlling and designing metallic contacts for molecular electronic systems.

Temperature Dependent Studies

The phenomenon of metal penetration through SAMs to the underlying SAM/Au interface has been observed for several metal-SAM systems including Al with $-CH_3$ and $-OCH_3$ terminated SAMS. The penetration mechanism is believed to occur via the creation of thermally-activated transient defects. At room temperature, we propose that metal-alkanethiolates moieties diffuse around the surface allowing the penetration of metal atoms to the Au/S interface. At low temperatures (<100 K), the formation of defects is believed to cease and thus penetration of metal atoms will stop.

To test this model and explore the substrate temperature dependent behavior further, we have developed and built a cryogenic sample stage capable of attaining 90 K in the time-of-flight secondary ion mass spectrometer. Figure 1 shows an image of the stage. The stage consists of a base which is cooled by flowing liquid nitrogen, and helium-refrigerator cooled moving "lock blocks" which engage the sample on each side. The stage can also be heated to temperatures in excess of 400 K by flowing heated nitrogen gas through the base. The stage is housed in a differentially pumped vacuum chamber mated to our current instrument. At present, we are also designing and installing cryogenic sample holders for the IR and XPS instruments.

Transition

Our results are very relevant to both molecular electronic technologies, and other areas, such as metal corrosion prevention. Our work has been of great interest to the Molecular Electronics Corporation, which operates adjacent to our laboratories in the Pennsylvania State Innovation Park, and to the DARPA molecular electronic teams. We have discussed both our results and future plans with these groups, who have made many suggestions about which metal/organic systems to consider.

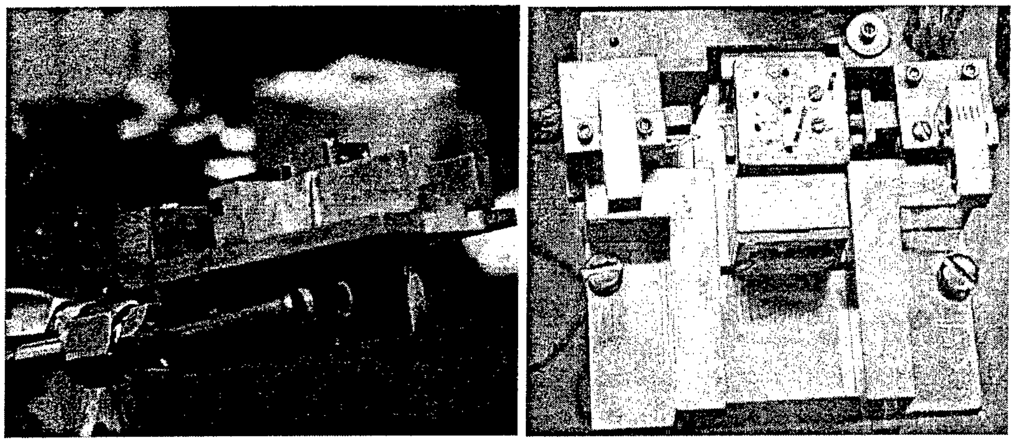


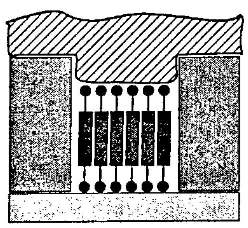
Figure 1: The new cryogenic stage for low temperature studies of metal/SAMs chemistry. The left image shows the side view of the stage exposing the base through which liquid nitrogen flows. The right image shows the top of the stage with the movable "lockblocks" which are coupled to a helium refrigerator.

PENNSTATE

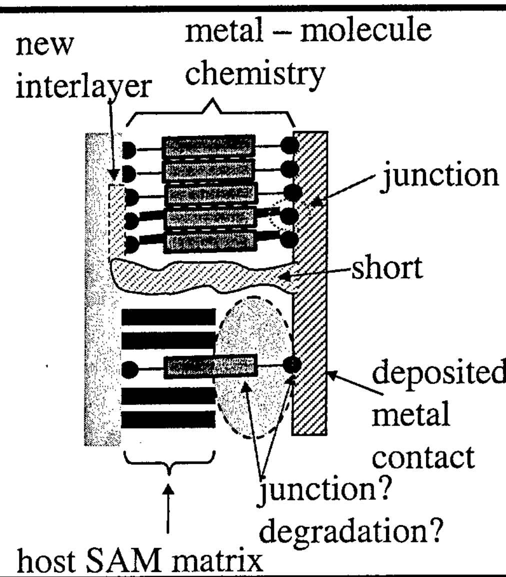
Mechanisms of Metal Contact Formation on Molecular Films

Nicholas Winograd, David L. Allara, The Pennsylvania State University, University Park, PA

Metallization Issues



"Nanopore"
Structure



Objective

•Reliable formation of molecular electronic devices for low power, Naval applications.

Approach

•Multiple surface - sensitive techniques.

Accomplishments

•Discovered novel metal – organic interaction; optimized for device contacts.

•Elucidated chemical reaction pathways of metal atoms deposited onto $-OCH_3$ functionalized SAMs and molecular wires

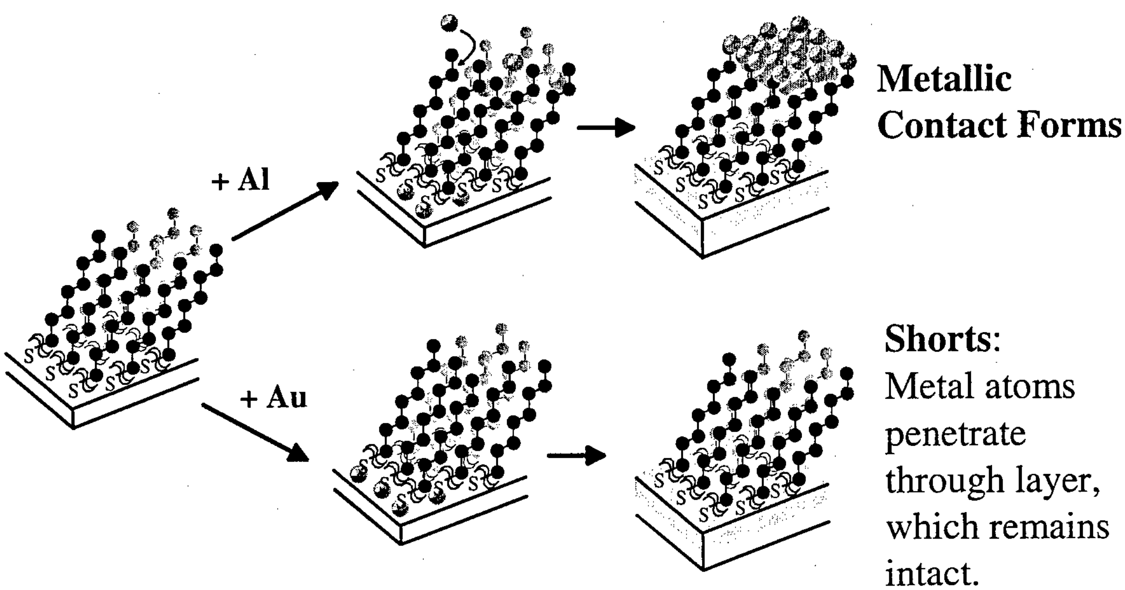
Impact

•Molecular electronics and optoelectronic devices for low power applications.

•Determine suitable architecture of novel 3D electroactive assemblies.

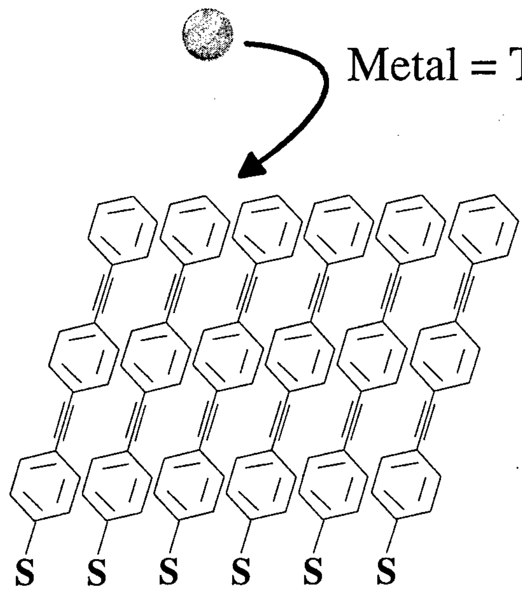
1. Interaction of Metals with a $-OCH_3$ Terminated SAM: A Test System

Metal	Shorts?	Metallic Contact Forms?
Ti	Destroys Molecule	
Ca		
Mg	No	Yes – but has a very low sticking probability
Al	No - but one layer of Al on top of Au	Yes
Cu	Yes	No
Ag	Yes	No
Au	Yes	No



2. Interaction of Metals with a Molecular Wire

Metal = Ti, Au, Cu, Al, Cr, Ag, Fe



Au

"Molecular Wire" – Basis for molecules which act as RAM memory

Metal	Shorts?	Metallic Contact Forms?
Ti	Destroys Wires	
Al	No - but one layer of Al on top of Au	Yes
Cu	Yes	No
Ag	Yes	No
Fe	No	Yes
Cr	Destroys Wires	
Au	Yes	No

Publications resulting from ONR support

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